BOSTON UNIVERSITY

GRADUATE SCHOOL

Dissertation

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Submitted in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy

[illegible]

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Dissertation

DETERMINATION OF THE WAVE-LENGTHS OF CERTAIN LINES BETWEEN LAMBDA 4156.633 and 4379.399 IN THE SECONDARY SPECTRUM OF HYDROGEN

by

Albert Alexander Kildare

(S.B., Boston University, 1921; A.M., Boston University, 1927)

submitted in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy

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OUTLINE

DETERMINATION OF THE WAVE-LENGTHS OF CERTAIN LINES BETWEEN LAMBDA 4156.633 AND LAMBDA 4379.399 IN THE SECONDARY SPECTRUM OF HYDROGEN.

INTRODUCTION.

A. The purpose of the investigation.

With the advent of atomic physics toward the close of the last century, many investigators centered their efforts on hydrogen on account of its simplicity of structure. At that time investigations of the hydrogen spectrum were confined chiefly to the Balmer series, which is due to atomic excitation. However, it has long been known that there is another spectrum of hydrogen which, on account of its complexity, has rendered analysis very difficult, and it is only in comparatively recent years that any headway has been made in the analysis[1] of this spectrum.

This spectrum, according to Merton[2], has introduced so many complications into theoretical investigations that it is impossible to dismiss the matter on the grounds that it is merely confined to molecular excitation. As a matter of fact Fabry and Buisson[3] have pointed out that the line series spectrum of hydrogen is not due to atomic excitation alone, but also to molecular excitation. In view of the large number of lines in this spectrum, therefore, progress in analysis can only be made with lines that are accurately determined. The purpose of this investigation, then, is to set up the necessary experi-

1. Richardson, O. W., and Tanaka, T., Proc. Roy. Soc., 107, p. 602, 1925
2. Merton, T. R., Proc. Roy. Soc., 97, p. 307, 1920
3. Fabry and Buisson, Journal de Physique, 2 p. 442, 1912

mental apparatus for photographing the lines at the greatest possible dispersion, thus permitting their measurements with greater accuracy than has been done heretofore.

B. Review of Investigations of the Spectrum of Hydrogen.

a. The Line Series Spectrum of Hydrogen.

As has been already stated, theoretical investigations were confined chiefly to the atomic spectrum because of the part it plays in the interpretation of atomic structure and behavior. In 1884 Balmer[1] discovered the series named after him, which is confined largely to the visible region. In 1908 Paschen[2] discovered another series in the infra-red, which was followed in 1914 by the discovery of the existence of a similar series in the ultra-violet by Lyman.[3] Since Paschen's discovery several other series have been added by Brackett,[4] Pfund,[5] and Poetker.[6]

b. The Secondary Spectrum of Hydrogen.

On account of the success attained in the analysis of the atomic spectrum of hydrogen as contrasted with the scant results obtained in attempts to analyze the secondary spectrum, recent experimental investigations are now, and have been for some time, concentrated on the molecular spectrum. The work of Merton and Barratt[7] is about the first complete and outstanding investigation in this field. In this investi-

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1. Balmer, J. J., Ann. d. Phys. und Chem. 25, p. 80, 1885
2. Paschen, F., Ann. d. Phys. 27, p. 537, 1908
3. Lyman, T., Nature, 93, p. 241, 1914
4. Brackett, F. S., Astrophys. J. 56, 154, 1922
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6. Poetker, A. H., Phys. Rev. 30, p. 418, 1927
7. Merton and Barratt, Roy. Soc. Phil. Trans. 222, p. 369, 1922

gation a number of lines were measured under such conditions that were most favorable for the production of the secondary spectrum. This work was then followed by that of Gale, Monk and Lee[1], and by the recent work of Finkelnburg[2]. In the meantime many other investigators had been engaged in experimental attempts to measure the lines of the secondary spectrum of hydrogen more accurately. Among them are Allibone[3], Poetker[4], Tanaka[5], Deodhar[6] and Connelly[7].

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1. Gale, Monk and Lee, Astrophys. J. 67, p. 89, 1928
2. Finkelnburg, W., Zs. f. Phys. 52, p. 27, 1928
3. Allibone, J. E., Proc. Roy. Soc. 112, p. 196, 1926
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7. Connelly, F. C., Phys. Soc. Proc. 42, p. 28, 1928-1930

II. DISCUSSION OF THE EXPERIMENT.

A. Description of the Apparatus.

a. The Discharge Tube and Its Operation.

In order to obtain a good molecular spectrum with a reasonable number of lines of sufficient intensity, several factors must be considered. Among the most important of these factors are current density, pressure, temperature and the removal of water vapor.

It is now generally known that the secondary spectrum of hydrogen is greatly enhanced if the gas is pure and free from water vapor. On the other hand, the presence of water vapor tends to suppress the secondary spectrum and enhance the Balmer series. In some cases, depending upon the region that is being photographed, the presence of certain gases[1], such as helium and argon, will greatly enhance the secondary spectrum in that region. However, current density plays a greater part in increasing the intensity of the lines. In his experiments Finkelnburg[2] observed that the greater the current density the greater will be the intensity of the weaker and weakest lines. By using a discharge of the highest possible current density he was able to obtain a large number of lines. However, too many lines add to the complexity of the spectrum and thereby increase the difficulty of analysis. Furthermore, the tube may not be able to hold out under the high temperature which accompanies large current density. Of the remaining factors pressure is the more important. Many investigators[3] have shown that variation in the pressure will produce appreciable change in the inten-

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1. Barratt, S., Phil. Mag. 46, p. 627, 1923
2. Finkelnburg, W., Zs. f. Phys. 52, p. 29, 1928
3. Goos, F., Zs. f. Phys. 31, p. 229, 1925; Bay and Steiner, Zs. f. Phys. 59, p. 48, 1929

sity of the spectrum. It is also evident that an optimum pressure must be established for each of the three main regions of the spectrum-- ultra-violet, visible, and infra-red-- if best results are to be obtained in any of them. Though variation of the temperature[1] will produce variation in the intensity of the spectrum, it is of more importance to keep the temperature reasonably constant once optimum operating conditions are established. The problem, therefore, was to design a suitable tube which would hold out under best experimental conditions for long periods of continuous operation, and at the same time give a reasonable number of lines.

Because of the various experimental conditions under which the tube must operate, its design proved to be one of the most important features of the entire apparatus. The discharge tube[2] used in this investigation is shown in the diagram below. It consists of an inner platinized quartz tube T, about 60 centimeters long with an internal diameter of 8 millimeters, and is surrounded by a water jacket of pyrex glass [illegible], which is 45 centimeters long and 5 centimeters in diameter. The quartz tube has, at the forward end, an enlarged cylindircal section which is 12 centimeters in length and about 3 centimeters in diameter. This section serves as a chamber for the aluminium electrode [illegible], which is 10 centimeters long and 2.6 centimeters in diameter. An outlet tube, which is blown on the enlarged section has a ground glass joint, and connects the discharge tube directly with the high vacuum system. This enlarged front end is closed by means of a cemented quartz window through

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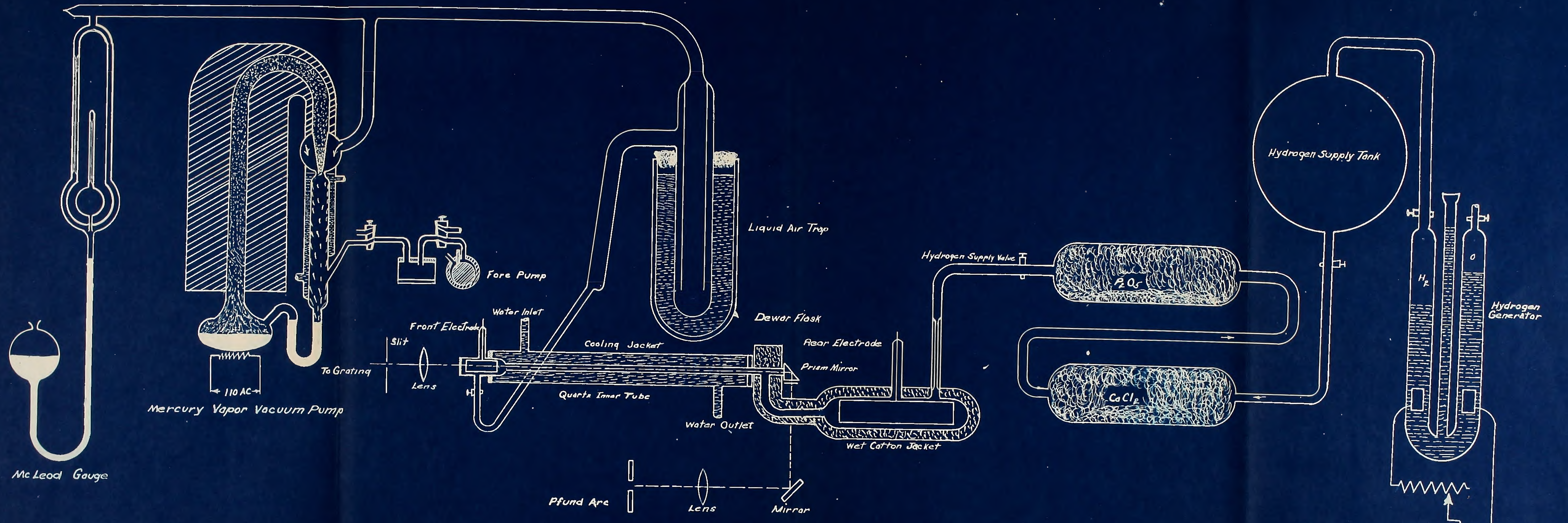
1. McLennan, Smith and Collins, Proc. Roy. Soc. 116, p. 277, 1927
2. Bay and Steiner, Zs. f. Phys. 45, p. 337, 1927



ARRANGEMENT OF APPARATUS

which the discharge is viewed end-on.

The rear end of the tube has the same uniform diameter, 8 millimeters, as the rest of the tube. A few centimeters from this end a side tube with a ground joint is blown. The purpose of this tube is to lead the discharge to the rear electrode chamber which is made of pyrex glass. This particular arrangement makes it possible to reflect the light back into the tube by covering the face of the prism parallel to the axis of the tube with a mirror, which results in increasing the intensity within the narrow core. If an enlarged electrode chamber similar to that of the front end were used here, intensity would not only be lost because of the impossibility of getting the mirror close enough to the narrow core, but also through absorption in the larger chamber.

The rear electrode chamber which is connected to the quartz tube by means of a ground glass joint presented many difficulties before a suitable one was designed. The main difficulties, however, were due to lack of cooling of this electrode and to a porous condition of the pyrex glass which results after the tube has been in operation for several hours. This porous condition is due to the sand blast action of the ions. These difficulties were overcome by slightly changing the design and making it much larger than before. This chamber is 20 centimeters in length and 5 centimeters in diameter, with the aluminium electrode, 15 centimeters long and 4.5 centimeters in diameter, which is closed at one end, thus making it cup-shaped. This increased size of the electrode afforded sufficient surface area to take care of any excess heat that may develop during long continuous periods of operation. Extra precaution, however, was taken to cool the electrode further by wrapping

it with absorbent cotton and allowing water to drip slowly over it.

The purpose of platinizing the inner surface of the tube is to increase the intensity of the molecular spectrum. Like every metal surface, it increases the rate of formation of the hydrogen molecules from the hydrogen atoms, thereby increasing the intensity of the secondary spectrum. It was also hoped that this platinum coating would serve to increase the intensity further by acting as a mirror, thus reflecting the light back into the central core of the tube. However, it is questionable whether the intensity gained in this manner is of any great magnitude. During the first two preliminary runs the tube was given a continuous coating of silver. However, after two or three hours of operation the silver coating disappeared almost completely. This occurred in each case, in spite of the fact that a heavy coating of silver was deposited on the inside of the tube. This single platinum coating has been subjected to more than thirty hours of operation for four to five hours at a time, without any apparent decrease in the amount of its distribution over the inner surface of the tube. The use of platinum, therefore, shows a distinct advantage in that it lasts longer than silver.

An Acme transformer was used to operate the tube. This transformer is capable of producing in the secondary an alternating current of 15000 to 30000 volts and 250 milliamperes when a current of 110 to 220 volts and 35 amperes is placed on the primary. As is shown in the diagram, the hydrogen is generated electrolytically and stored in a large supply vessel which has a capacity of about 5 liters. From the supply flask the hydrogen gas is then passed through drying tubes of calcium chloride and phosphorus pentoxide before being introduced into

the discharge tube. Sealed into the inlet tube is a small capillary which retards the rate of flow of the gas. In addition to the capillary, the regulation of the rate of flow of the gas is accomplished by means of the stopcock in the generating system and a variable resistance in the circuit of the electrolytic generator. To do this the stopcock must first be adjusted, and then the resistance so varied as to produce a constant stream of hydrogen at the desired pressure. In this manner, once optimum pressure is reached there is little or no difficulty in maintaining it. The hydrogen may also be fed into the tube intermittently at periods of one to two hours apart. When this method is used the pressure must be constantly observed, and it is well to view the spectrum during exposure from time to time. As the rear end of the tube is closed by means of a small right prism the discharge may be conveniently viewed by means of a direct vision spectroscope in order to determine any change that may take place in the spectrum.

On two occasions the discharge was observed with the direct vision spectroscope, when hydrogen was fed into the tube intermittently. Hydrogen was introduced into the tube at a pressure slightly above .15 mm of mercury and the tube cut off completely from both the generator system and the exhaust system. The discharge was then observed under these conditions. Shortly after the vacuum system was cut in. After a few minutes the discharge glowed brightly and a brilliant molecular spectrum was obtained. This spectrum was examined for at least an hour without any apparent change in the intensity. So great was the intensity of the spectrum that the lines could be plainly seen at a slit-width of .035 mm. This method of introducing the hydrogen is evidently well

suited for exposures of short duration.

The high vacuum system is also shown in the diagram. From the front end of the quartz tube the outlet tube is directly connected with the liquid air trap. The purpose of this trap is to prevent any mercury vapor or other impurities in the vapor state from diffusing into the hydrogen discharge tube. The mercury vapor pump is of the Langmuir type, and is connected with a rotary fore pump of the Cenco design. Connected in the system with these pumps is an accurately calibrated McLeod gauge for the determination of the pressure from time to time.

b. The Pfund Iron Arc as a Comparison Spectrum.

The standard Pfund arc as recommended by the International Astronomical Union was used for the comparison spectrum. This arc was operated at 220 volts and 4 amperes at a length of 15 mm. This was magnified about ten times by means of the lens shown in the diagram and brought to a focus on one of the faces of the small prism at the rear end of the tube. As the light from the arc was directed through the tube to the slit, the rear bore of the tube served as an aperture. Therefore less than 1 cm. of the 15 cm. image was used. This assured uniform intensity distribution and freedom from broadening of the lines which is due to the pole effect.

In order to conveniently direct the beam of light from the arc through the tube, the small right prism was used to close the rear end of the tube. From the Arc the beam was passed through the lens to the mirror and then to the prism. From here it was reflected through the tube to the slit. The lens in front of the discharge tube is used to focus both sources on the slit. The grating is of the Littrow type of speculum metal and is used with a 30 foot lens. The

ruled surface of the grating is 5 by 3.75 inches and contains 14,500 lines to the inch.

B. The Photography and Measurement of the Lines.

As has been pointed out before, maintenance of an optimum pressure within the tube and constant temperature, particularly within the box housing the grating, are absolutely necessary if good photographs of the lines are to be obtained. In order to establish the desirable pressure, which was measured by a McLeod gage, the tube was operated from two to three hours before any exposures were made. During this time the pressure was frequently observed and the rate of flow of the hydrogen gas adjusted until the necessary pressure condition reached. This condition could be readily determined by examining the discharge by means of a direct vision spectroscope. Once this pressure was reached it could be maintained for several hours by merely adjusting the variable resistance in the generator system. Each plate photographed in this investigation was exposed for from three to four hours. At no time during this interval was the pressure variation greater than .05 cm. of mercury.

To maintain a constant temperature the grating room was thermostatically controlled. In addition to the thermostat in the grating room, another was placed in the housing of the grating. During the various times of exposure the thermostat in the room varied about .2 degrees Fahrenheit while the one in the grating box varied less than .1 degree Fahrenheit.

In addition to the control of the temperature and pressure, the elimination of vibrations is also essential. The laboratory in which the experiment was carried out is so built as to reduce vibration to a

minimum. The floor upon which the grating and slit supports, and other apparatus rest is of the so-called floating type; that is, it is not directly connected with the walls of the room or the external walls of the building. In addition, a second floor is suspended from the walls of the room in the vicinity of the discharge tube and the slit. This precaution is taken in order to eliminate any vibrations that may be caused by walking during the exposures. An idea of the arrangement of the apparatus may be obtained from the photograph of the room shown below.

The region from lambda 4156.633 to lambda 4379.399 was photographed on Eastman spectroscopic plates which are very sensitive to this region. Of the four plates made in this investigation the first plate showed a fairly strong continuous spectrum which may be due to hydrogen. During the exposure of this plate it was quite difficult to maintain a low pressure. With the other plates, where lower and a more constant pressure was maintained, the continuous spectrum[1] appeared less pronounced. This was particularly true of the last two plates where lowest and best pressure conditions were maintained.

Before each plate was measured it was brought to constant temperature in the thermostatically controlled comparator. This comparator is built in a heat insulated case, through the cover of which the telescope projects. The wire diagram of the comparator is shown below.

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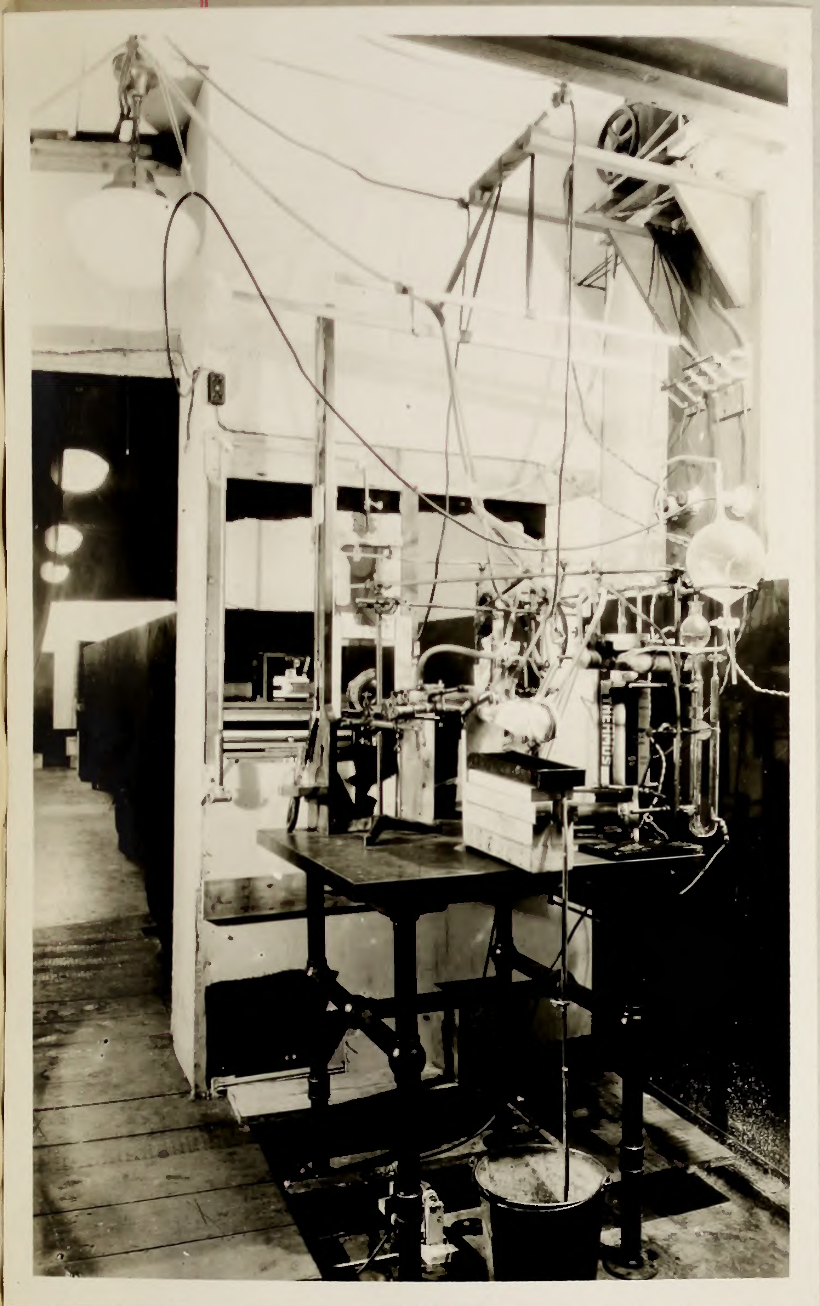
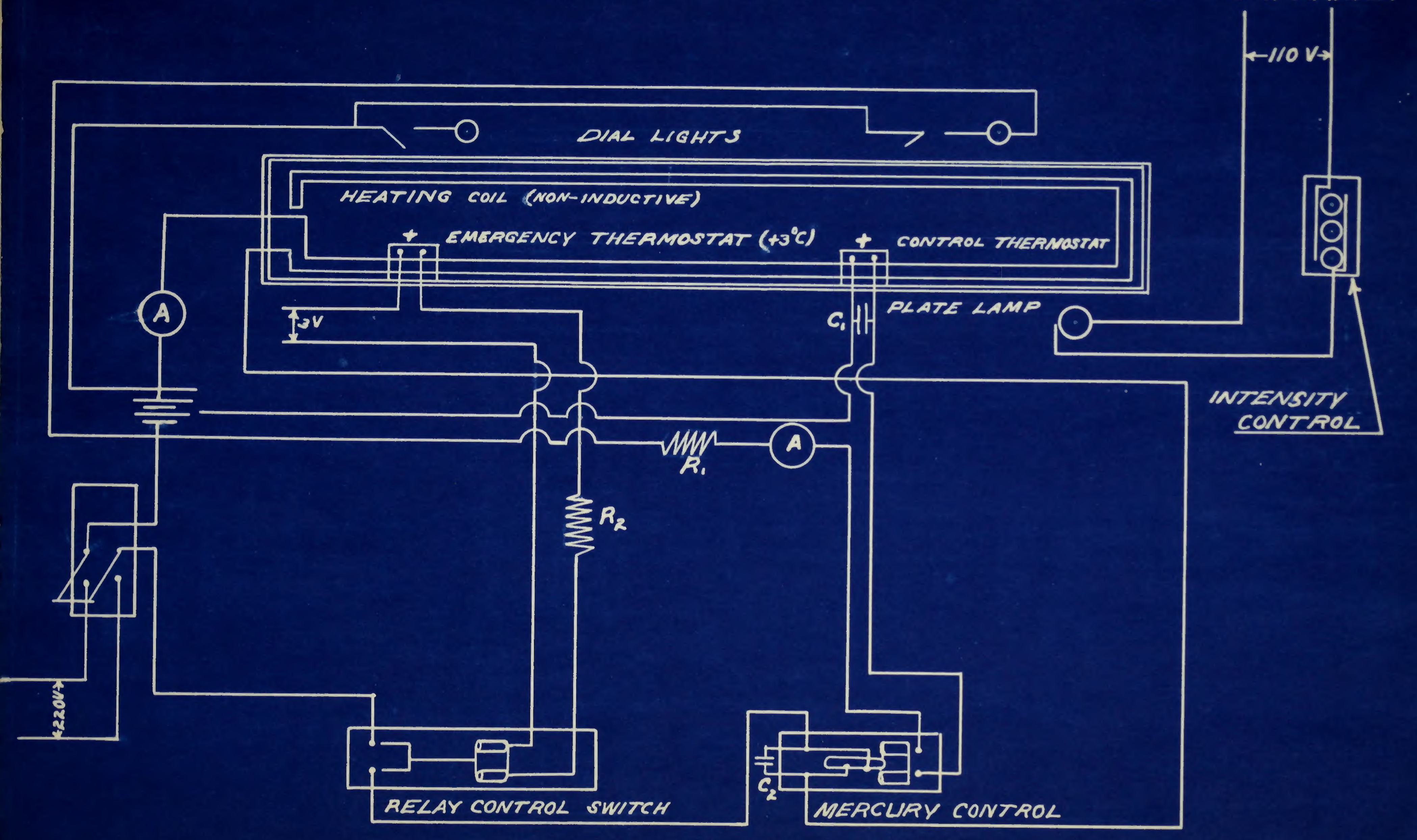
1. Merton and Barratt, <u>Phil. Trans</u>. 222, p. 369, 1922



Photograph of room showing
arrangement of the apparatus.

THE WIRE DIAGRAM OF THE CONSTANT TEMPERATURE COMPARATOR



III. DISCUSSION OF RESULTS

A. Comparison of Results with Measurements of Other Investigators.

In Table I the results of measurements of the same lines taken from three difference plates are given. Each plate was measured twice, first from red to violet and then from violet to red. This was done to eliminate any personal error in the setting of the comparator. The mean values for each plate are given in the first three columns of the table, while the last column shows the mean of these values for each line measured. The intensities given are estimates based on how the lines appear to the eye. They give only a rough idea of the quality of each line. The symbol 0^4 is the lowest estimate given, and indicates that the line is just seen on the plate and is barely measurable. As the apparent intensities of the lines increase they are designated by 0^3, 0^2, 0, 1, 2, etc. up to 10. No attempt is made to estimate intensities beyond 10 as there seems to be no particular reason for doing so.

In Table II a comparison of the measurements with those of other investigators is given. In this comparison the results of Gale, Monk and Lee, and of Finkelnburg were used, as the works of these investigators, together with that of Merton and Barratt, represent the most thorough investigations of the secondary spectrum of hydrogen. Furthermore, the works of Gale, Monk and Lee, and Finkelnburg are more recent than that of Merton and Barratt, and the values of the wave-lengths are given to a greater number of significant figures.

In the first column of Table II the mean values of the measurements are given followed by the estimated intensities. The intensities of Gale, Monk and Lee, and of Finkelnburg were not given as they serve no

Table I. Measurements of Wave-lengths from
Lambda 4156.633 to Lambda 4379.399

Plate				
36	37	38	Int.	Mean
4156.629	.636	.636	0	.633
56.850	.857	.850	0^4	.853
61.939	.943	.946	0^2	.943
63.598	.600	.610	0^3	.602
65.188	.193	.198	0^3	.193
71.296	.306	.311	8	.304
75.150	.160	.160	0	.157
77.110	.114	.112	10	.112
77.715	.728	.723	0	.722
79.594	.594	.591	0^2	.593
80.105	.106	.108	2	.106
82.169	.170	.166	3	.168
95.676	.673	.679	4	.676
99.793	.803	.788	2	.795
4200.981	.965	.982	0^3	.976
05.102	.102	.099	10	.101
06.100	.102	.097	0^2	.099
09.174	.184	.179	0^2	.179
10.140	.140	.134	2	.137

Table I cont'd. Measurements of Wave-lengths from
Lambda 4156.633 to Lambda 4379.399

	Plate			
36	37	38	Int.	Mean
12.506	.508	.502	7	.505
22.167	.169	.174	0	.171
22.521	.534	.532	1	.529
23.955	.954	.948	0	.952
33.436	.434	.426	0^3	.433
43.354	.357	.372	0^4	.361
4303.437	.435	.440	0^2	.438
03.858	.895	.875	0^4	.876
06.283	.283	.267	0^3	.278
27.935	.937	.938	0^3	.937
32.622	.621	.643	0^4	.629
35.527	.519	.529	0^4	.525
40.466	.464	.471	10	.468
54.551	.542	.554	0^4	.549
58.---[1]	.338	.336	0^4	.337
79.408	.396	.393	0	.399

1. This line was too faint to be properly measured.

Table II. Comparison of Results with Those of Other Investigators.

Mean value of measurements	Intensity	Gale, Monk and Lee	Finkelnburg	Mean value[1]	Deviation
4156.633	0	.633	.633	.633	.000
56.853	0^4	.861G	.873	.867	-.014
61.943	0^2	.941	.949	.945	-.002
63.602	0^3	.605	.608	.607	-.005
65.193	0^3	.195	.188	.191	+.002
71.304	8	.308	.309	.308	-.004
75.157	0	.165	.163	.164	-.007
77.112	10	.125	.113	.119	-.007
77.722	0	.720	.718	.719	+.003
79.593	0^2	.598	.591	.594	-.001
80.106	2	.111	.105	.108	-.002
82.168	3	.170	.166	.168	.000
95.676	4	.674	.668	.671	+.005
99.795	2	.793	.787	.790	+.005
4200.976	0^3	.971G	.959	.965	+.011
05.101	10	.098	.102	.100	+.001
06.099	0^3	.085	.091F	.088	+.011
09.179	0^2	.169	.175	.172	+.007
10.137	2	.131	.129	.130	+.007

Table II cont'd. Comparison of Results with Those of Other Investigators.

Mean value of measurements	Intensity	Gale, Monk and Lee	Finkelnburg	Mean value[1]	Deviation
12.505	7	.498	.507	.502	+.003
22.171	0^2	.158	.160 F	.159	+.012
22.529	1	.518 G	.514	.516	+.013
23.952	0	.935	.941 F	.938	+.014
33.433	0^3	.407	.408	.407	+.026
43.361	0^4	.326	.348	---	---
4303.438	0^2	.423	.437	.430	+.008
03.875	0^4	.877	.849	.---	-.002G
06.278	0^3	.276	.273	.275	+.003
27.937	0^3	.927	.939	.933	+.004
32.629	0^4	.619	.628	.624	+.005
35.525	0^4	.519	.532	.526	-.001
40.468	10	.470	.466	.468	.000
54.549	0^4	.540	.478	---	+.009G
58.337	0^4	---	.344	---	-.007F
79.399	0	.403	.397	.400	-.001

1. This column gives the mean values of Gale, Monk and Lee and of Finkelnburg.

particular purpose here. In the last column the deviations of the measured wave-lengths from the mean values of these investigators are

given. In a few instances the measured wave-length was compared with one or the other of the individual values. Whenever this was done no proper mean was possible on account of great differences in their values. The line was then compared with one of the values with which it most closely agrees. Such a comparison is indicated by the letters F or G following the deviation, and signifying that the line was compared with the value of Finkelnburg or Gale, Monk and Lee. When the deviation from the mean value exceeded 10 parts in 1×10^6, the line was compared with one or the other of the values of these investigators. In every such comparison the deviation of the measured value fell within 10 parts in 1000. Such comparisons are indicated by the letters F or G following the individual value with which it was compared.

An examination of the table shows that deviations greater than 11 parts in 1×10^6 are not many. In one case - that of the line 4233.433 - the measured value shows a wide variation both from the mean value and the individual values. This great variation is probably due to the interference of an iron line, as one is in the vicinity of this line. In the case of the line 4243.361, the differences existing between the individual values as well as between the measured value were so great that no proper comparison could be made. Generally, however, the measured wave-lengths show good agreement with the mean values of these investigators, and whenever this was not possible, good agreement could be obtained with one or the other of the individual values in many cases. This must be attributed to the fact that the lines were photographed at a fairly high dispersion, namely, about 0.889 A.U.per millimeter.

IV. SUMMARY

1. The most favorable conditions for the production of the secondary spectrum of hydrogen are discussed.

2. A description of the discharge tube and other parts of the apparatus is given.

3. The nature of the source and the comparison iron arc is described.

4. The conditions under which the lines were photographed and measured are discussed.

5. A comparison of the result with those of other investigators is given.

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VI. AUTOBIOGRAPHY

I was born in Kingston, Jamaica, B. W. I., on the sixteenth day of December, 1897. My father, George Walter Kildare, died October 5, 1902. My mother, Jane Clark Kildare, died November 19, 1913. I am the last of nine children.

I first attended the Mico elementary school of Kingston and St. Andrews, Jamaica, from 1905 to 1911. In May, 1911, my mother brought me to America. In America I have attended the following schools and colleges during the periods specified, and received the degrees indicated: Dwight Grammar School of Boston, Mass., 1911-1912; Boston English High School, 1912-1916; the College of Liberal Arts of Boston University, 1916-1921, S.B.; the Graduate School, 1926-1927, A.M.; the University of Chicago, 1931-1932, and Boston University, 1932-1934. This brief survey of my educational opportunities would not be complete without mention of my unofficial connection with the Massachusetts Institute of Technology where I have been working for the past year, and where I have benefitted educationally during the course of my work.

Since 1921 I have been engaged in teaching primarily in the South and have taught in the following institutions: Virginia State College, Ettrick, Va., 1921-1926, Wilberforce University, Wilberforce, Ohio, 1927-1928, and Lincoln University, Jefferson City, Mo., 1928-1931.